

Preparation of carbon-coated $W_{18}O_{49}$ and its photoactivity under visible light

Fumi Kojin ^a, Masanobu Mori ^b, Yumiko Noda ^b, Michio Inagaki ^{a,*}

^a Faculty of Engineering, Aichi Institute of Technology, Yakusa, Toyota 470-0392, Japan

^b Faculty of Engineering, Gunma University, Tenjin-cho, Kiryu, Gunma 376-8515, Japan

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Abstract

Carbon-coated $W_{18}O_{49}$ powders were prepared from the mixture of *para*-ammonium tungstate with poly(vinyl alcohol) by heat treatment in inert atmosphere at a temperature between 750 and 900 °C for 1 h. The synthesized $W_{18}O_{49}$ crystals had prismatic morphology in small size, less than 0.5 μm in diameter and about 1 μm in length. Carbon-coated $W_{18}O_{49}$ was shown to have photoactivity under visible light irradiation by comparing the concentration changes of methylene blue, phenol and dimethylsulfoxide with time under the irradiation of visible light to that in the dark. Photoactivity of $W_{18}O_{49}$ was supposed to be due to the formation of OH[•] radicals on the basis of the degradation of dimethylsulfoxide, its quantitative transformation to methanesulfonic acid. Carbon coating seemed to have various roles: to reduce WO_3 to $W_{18}O_{49}$, to inhibit the sintering and crystal growth of $W_{18}O_{49}$ to keep them small size, and also to concentrate pollutants around $W_{18}O_{49}$ crystal by adsorption.

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1. Introduction

Various kinds of environmental pollutions have become serious for the human beings, such as pollution of environmental water by sick endocrine disrupters, air pollution by NO_x and SO_x exhausted from vehicles and factories, building syndrome by chemicals evaporated from synthetic building materials, etc. Photocatalytic decomposition of harmful organic compounds by using anatase-type TiO_2 is one of the effective methods to eliminate pollutants in air and water [1–5]. Now various building materials containing photoactive TiO_2 have been put on the market and many air cleaning equipments using TiO_2 has been seen at electronics stores, even though it is only active under ultraviolet (UV) irradiation. Since UV rays are contained only 4% in solar light, many efforts have been devoted to develop the photocatalysts, which are active under irradiation of visible light. Doping of light elements, such as C, S and N, and of metal ions, such as Cr, Ni, etc., into anatase-type TiO_2 was reported to give visible light activity [6–11].

Also different semiconductive compounds, such as $BiNO_4$, $In_{1-x}Ni_xTaO_4$ and $TaON$, were reported to be visible light active [12–14]. Tungsten oxide WO_3 was also reported to be visible light active, but its practical application was pointed out to be difficult because of its high solubility to water [15].

We developed successfully a new photocatalyst, carbon-coated $W_{18}O_{49}$, which is active under visible light, and reported the preliminary results in our previous paper [16]. The preparation procedure was very simple; a mixture of *para*-ammonium tungstate with poly(vinyl alcohol) was heat-treated at 800 °C in inert atmosphere. The same procedure was applied to prepare different carbon-coated ceramic powders [17]. Carbon-coated TiO_2 with anatase phase gave certain success as photocatalysts, coupled with high adsorptivity [18–21]. New process was recently proposed to prepare porous carbons through the preparation of carbon-coated MgO followed by the dissolution of MgO by a diluted acid, which left nano-sized pores (mostly mesopores) [22–24]. Reduced phases of TiO_2 , i.e., Ti_nO_{2n-1} , were prepared through the interaction of the substrate TiO_2 with the coated carbon and were found to have photoactivity under visible light [25,26].

In the present work, the formation condition of carbon-coated $W_{18}O_{49}$ was studied in detail. Its photocatalytic activity

* Corresponding author. Tel.: +81 565 48 8121; fax: +81 565 48 0076.

E-mail address: ina@aitech.ac.jp (M. Inagaki).

was studied through the photodecomposition of methylene blue, phenol and dimethylsulfoxide in water.

2. Experimental

2.1. Preparation of carbon-coated tungsten oxide

para-Ammonium tungstate $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41}\text{H}_2\text{O}$ (PAT, reagent grade) and poly(vinyl alcohol) (PVA) were mixed in equal mass ratio in aqueous solution with 10 mass% concentration at 60 °C and then dried to be a powder mixture. In order to explore the formation condition of $\text{W}_{18}\text{O}_{49}$ from the mixture, it was heat-treated at a temperature between 700 and 1000 °C for 1 h in a flow of Ar. For comparison, the reduced phase $\text{W}_{18}\text{O}_{49}$ without carbon coating was also prepared from reagent grade WO_3 powder by heating in a flow of N_2 gas containing 3 vol% H_2 . Heating rate up to a programmed temperature was 5 °C/min and a flow rate of gases during heat treatment was 60 mL/min. Crystalline phases in the samples were identified from powder diffraction pattern of X-rays ($\text{Cu K}\alpha$). Optical diffuse reflectance spectrum of these powders prepared was measured using a spectrophotometer in a reflection mode.

In order to examine the process of pyrolysis of PAT, PVA and also their mixture, thermogravimetry was carried out at heating rate of 2 °C/min from room temperature to 1050 °C in Ar. From different temperatures on the course of heating, the sample was quenched to room temperature, and the crystalline phases formed in the samples were identified by X-ray diffraction. Apparent surface area on carbon-coated tungsten oxides was calculated from adsorption isotherm of N_2 at 77 K by BET method.

2.2. Photocatalytic activity

In order to evaluate photocatalytic activity, three model organic pollutants were selected, methylene blue $\text{C}_{16}\text{H}_{18}\text{N}_3\text{S}$ (MB), phenol $\text{C}_6\text{H}_5\text{OH}$ and dimethylsulfoxide $(\text{CH}_3)_2\text{SO}$ (DMSO). MB was commonly used in various papers to evaluate photocatalytic activity. In the case of MB, only color fading of its solution was followed, but the identification of its degradation products was not easy. Therefore, phenol and DMSO were used; for phenol, oxidation and degradation products, catechol, hydroquinone, formic acid, etc., could be detected [27] and DMSO was reported to be oxidized quantitatively by hydroxy radicals to form methanesulfonic acid $\text{CH}_3\text{SO}_3\text{H}$ (MSA) [28]. For carbon-coated tungsten oxides prepared in the present work, it was necessary to compare the concentration changes of these pollutants under irradiation of both UV and visible light with that in the dark, because of their high adsorptivity for these pollutants in the solution, as reported on other carbon-coated photocatalysts, TiO_2 and $\text{Ti}_n\text{O}_{2n-1}$ [18,25].

Into a 100 ppm MB solution of 300 mL, the carbon-coated tungsten oxide powder of 0.3 g was dispersed under stirring and then the solution was started to be irradiated either by UV rays from two black light lamps or by visible light from a fluorescent

lamp with a film cutting UV rays. At the surface of MB solution, the strength of UV rays was 0.9 mW/cm² in the wavelength range of 220–300 nm and that of visible light was 18 W/cm² in the wavelength range of 400–700 nm. The concentration of MB in the solution was determined as a function of irradiation time from absorbance change at a wavelength of 664 nm using a spectrophotometer. The same experiment was carried out also in the dark on the samples to evaluate the adsorptivity of catalyst particles.

For oxidation and photodegradation of phenol, carbon-coated tungsten oxide prepared at 800 °C, which showed relatively high photoactivity for MB decomposition, was used. The result was compared with those on commercially available WO_3 and $\text{W}_{18}\text{O}_{49}$ prepared from WO_3 in the H_2 -containing N_2 gas flow. The sample powder of 0.1 g was dispersed to either 1 or 10 ppm phenol solutions. The solution was irradiated by visible light from a fluorescent lamp. The time trend of phenol concentration was measured by a high performance liquid chromatography (HPLC) with UV detection (254 nm), which consisted of ODS packed column as a separation column and 30% methanol/70% water as mobile at 0.3 mL/min of flow rate. The same experiment was also performed on the samples in the dark. Degradation products from phenol were detected by electrospray ionization-mass spectrometry (ESI-MS; Shimadzu-LCMS2010A) with negative ionic mode.

For DMSO degradation, carbon-coated tungsten oxide prepared at 800 °C of 0.1 g was dispersed to 10 ppm DMSO solution. The solution was irradiated by visible light. The time trends of the decrease in DMSO concentration and the increase in the degradation product MSA were measured by reversed phase HPLC with UV detection and suppressed-type ion chromatography with conductivity detection, respectively.

3. Results

3.1. Formation and characteristics of carbon-coated $\text{W}_{18}\text{O}_{49}$

Change in XRD pattern with heat treatment temperature was shown for the mixture of PAT with PVA in Fig. 1. After 700 °C treatment, only weak diffraction peaks corresponding to $(\text{NH}_4)_{0.42}\text{WO}_3$ were detected and main part of the sample was reasonably supposed to be amorphous (Fig. 1a). After 800 and 850 °C treatment, the formation of reduced phases of WO_3 , $\text{W}_{18}\text{O}_{49}$ ($\text{WO}_{2.722}$ in composition) and WO_2 , was observed and relative amount of WO_2 to $\text{W}_{18}\text{O}_{49}$ increased with increasing heat treatment temperature (Fig. 1b and c). By heating to 900 °C, WO_2 became a principal crystalline phase, with a small amount of $\text{W}_{18}\text{O}_{49}$ remained (Fig. 1d). After 1000 °C treatment, even the formation of metallic W was detected, in addition to WO_2 as main phase.

Apparent BET surface area measured on carbon-coated tungsten oxide was about 40 m²/g, 45 m²/g for 800 °C-prepared sample and 26 m²/g for 900 °C-prepared one. Although the amount of carbon coated on TiO_2 was easily determined from ignition loss at a high temperature in air, the amount of carbon in the present samples was difficult to be determined

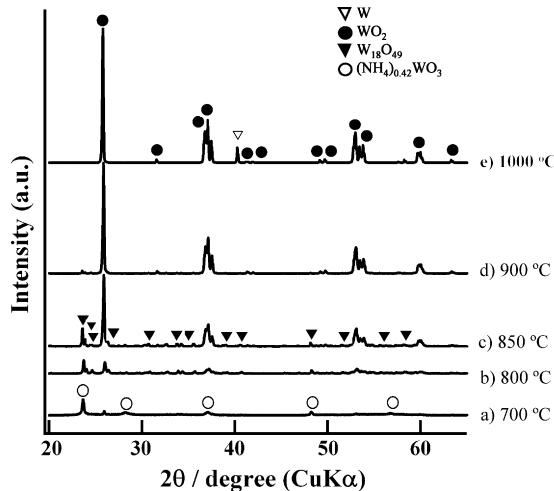


Fig. 1. XRD patterns of the products of the heat treatment of the mixtures of *para*-ammonium tungstate with poly(vinyl alcohol).

quantitatively, because the tungsten oxides W₁₈O₄₉ and WO₂ were also oxidized during combustion of carbon at a high temperature in air. So, the surface area for tungsten oxide and carbon-coated could not be estimated separately. However, it was experimentally proven by using MgO substrate that the carbon coated on MgO substrate was very porous [22–24]. In the present carbon-coated tungsten oxide, therefore, the coated carbon is reasonably supposed to be porous by taking account of large mass difference between carbon and tungsten, even though apparent BET surface area is not large.

SEM image of carbon-coated tungsten oxides prepared at 800 °C in Ar is compared with that of W₁₈O₄₉ prepared at 900 °C in H₂-containing N₂ gas in Fig. 2. In carbon-coated tungsten oxides, two kinds of particles with different morphology are observed, round particles and prismatic ones (Fig. 2a). By comparing with W₁₈O₄₉ without carbon coating (Fig. 2b), it is proven that prismatic particles are W₁₈O₄₉. Round particles were supposed to be WO₂, because the same morphology was observed on the sample heated up to 1000 °C, of which the principal tungsten oxide was known to be WO₂.

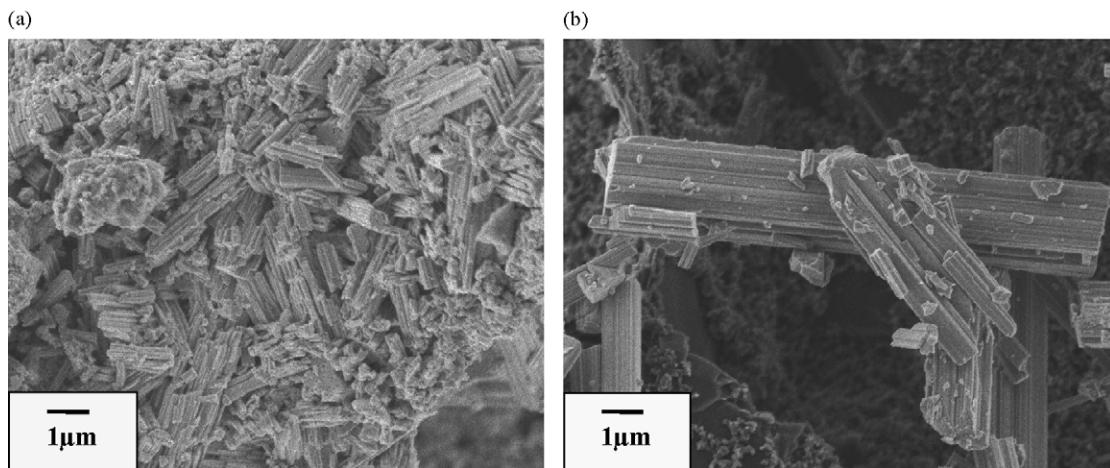


Fig. 2. FE-SEM images of carbon-coated W₁₈O₄₉ prepared PAT/PVA mixture at 800 °C (a) and W₁₈O₄₉ prepared from WO₃ in reducing atmosphere without carbon coating (b).

(Fig. 1e). It has to be pointed out here that particle size of carbon-coated W₁₈O₄₉ is small, less than 0.5 μm in diameter and about 1 μm in length, much smaller than W₁₈O₄₉ without carbon coating (Fig. 2a).

The carbon formed in this process was supposed to be amorphous. This is the reason why no carbon was detected in XRD patterns (Fig. 1). Also it was supposed to be porous, as explained above. Most of the carbon formed is located on the surface of tungsten oxide particles, because the exactly the same process on the mixture of PVA and TiO₂ gave carbon-coated TiO₂, as reported in our previous papers [18–21]. In the present sample prepared at 800 °C (Fig. 1b), the particle with a thin sheath-like layer was occasionally observed after a slight pulverization.

In Fig. 3a, TG curves are shown for PAT, PVA and the mixture of PAT with PVA in the equal mass ratio. In Fig. 3b, XRD patterns of the PAT/PVA mixture quenched from different temperatures indicated on the TG curve for the mixture in Fig. 3a. TG curve of the PAT/PVA mixture shows weight change in three steps, at around 250, 400 and 800 °C. After the first weight loss, most part of PAT changed to aqmorphous solids due to departure of ammonia and only small amount was remained as crystalline phase of (NH₄)_{0.42–0.33}WO₃ (Fig. 3b). At the same time, PVA was pyrolyzed to carbonaceous fluid state and coated solid particles, most of which are supposed to be tungsten oxides in amorphous state. In the second step, further departure of ammonia and pyrolysis of carbonaceous layer on solid particles were proceeded. Since a single phase of W₁₈O₄₉ was obtained at 780 °C and very small weight loss after the 2nd step to the beginning of the 3rd step, the formation of W₁₈O₄₉ was known to occur at around 800 °C. In the 3rd step of weight loss, mostly carbonization of carbonaceous solid formed from PVA occurred, being associated with departure of hydrogen, which seemed to promote gradual reduction of W₁₈O₄₉ to WO₂, and even partly to metallic W.

In Fig. 4, optical diffuse reflectance spectrum of carbon-coated tungsten oxide prepared at 800 °C in Ar is compared to W₁₈O₄₉ prepared at 900 °C in H₂-containing N₂ gas and TiO₂ with anatase structure (commercially available photocatalyst

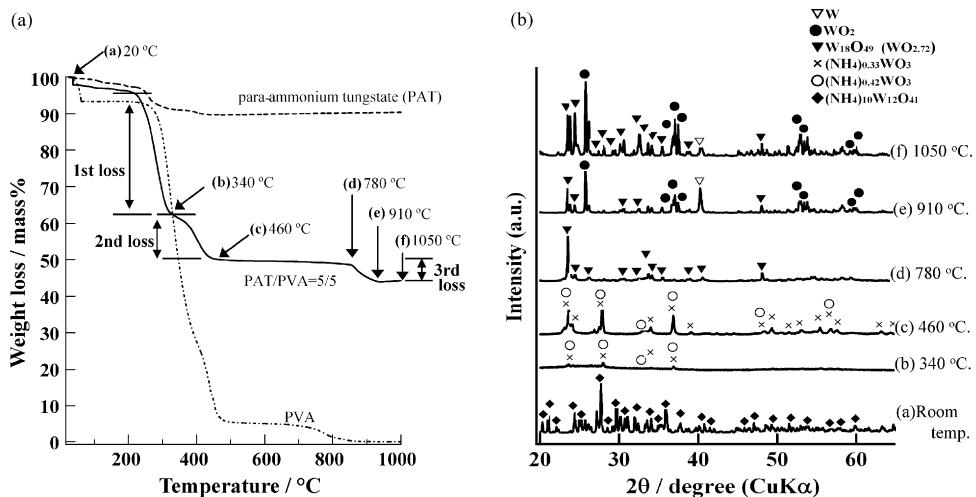


Fig. 3. (a)TG curves and (b) XRD patterns for the mixture of *para*-ammonium tungstate and PVA.

ST-01). ST-01 is known to be active only under UV rays and so have absorption in the wavelength range below 400 nm. However, the samples composed mainly of W₁₈O₄₉, both carbon-coated and without carbon coating, show absorption in the whole range of wavelength, including visible light. The spectrum of carbon-coated tungsten oxide containing W₁₈O₄₉ is supposed to comprise of overlapping two spectra, one due to carbon layer on the particles and the other due to W₁₈O₄₉, both can absorb visible light.

3.2. Photocatalytic activity of carbon-coated tungsten oxides

3.2.1. Photocatalytic degradation of MB

In Fig. 5, the changes in relative concentration of MB, c/c_0 , in the solution with time t under visible light and UV rays irradiation and also in the dark for carbon-coated tungsten

oxides prepared at 700–1000 °C for 1 h in Ar. On the sample prepared at 800 °C, the decrease in c/c_0 under UV irradiation cannot be differentiated from that in the dark, indicating that the degradation of MB is difficult to detect and only the adsorption of MB occurs. Under the visible light, however, the decrease in c/c_0 is much faster than other two conditions, showing marked degradation of MB under visible light. On the sample prepared at 850 °C, the decrease in c/c_0 with t is the fastest under visible light and that under UV is faster than that in the dark. On the sample prepared at 900 °C, decrease in c/c_0 under visible light is faster than those under UV irradiation and in the dark. On the other hand, both the samples prepared at 700 and 1000 °C show exactly the same behavior under three different conditions.

By taking into account the fact that the samples prepared at 800–900 °C contain W₁₈O₄₉ phase and those at 700 and 1000 °C consist of other phases (NH₄)_{0.42–0.33}WO₃ with amorphous phase and WO₃, respectively, it can be concluded that W₁₈O₄₉ phase is active under visible light. On the results shown in Fig. 5b–d, it has to be pointed out that the strength of visible light was much stronger than that of UV rays (18 and 0.9 mW/cm², respectively). Therefore, photocatalytic activity under UV irradiation was difficult to detect in the present condition of MB solution and also it cannot be compared quantitatively to that under visible light.

3.2.2. Photocatalytic oxidation and degradation of phenol

Since W₁₈O₄₉ was supposed to be visible light active in the previous section, the behavior of carbon-coated tungsten oxide prepared at 800 °C, which contained W₁₈O₄₉ phase, was compared under visible light irradiation with those of commercially available WO₃ powder and W₁₈O₄₉ prepared at 900 °C in reducing atmosphere (W₁₈O₄₉ without carbon coating). In Fig. 6, relative concentration of phenol, c/c_0 , was plotted against time t under visible light irradiation and in the dark under the suspension of the sample powder. Both WO₃ and W₁₈O₄₉ without carbon coating do not show the decrease both in the dark and under visible light irradiation. On the carbon-coated tungsten oxide prepared at 800 °C, however, c/c_0 decreases markedly in the dark and also under the irradiation of

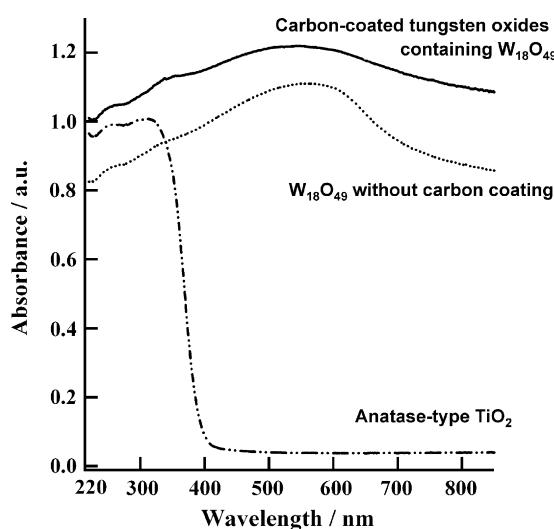


Fig. 4. Optical diffuse reflectance spectra of carbon-coated tungsten oxide containing W₁₈O₄₉, single phase of W₁₈O₄₉ prepared in reducing atmosphere, and commercially available anatase (ST-01).

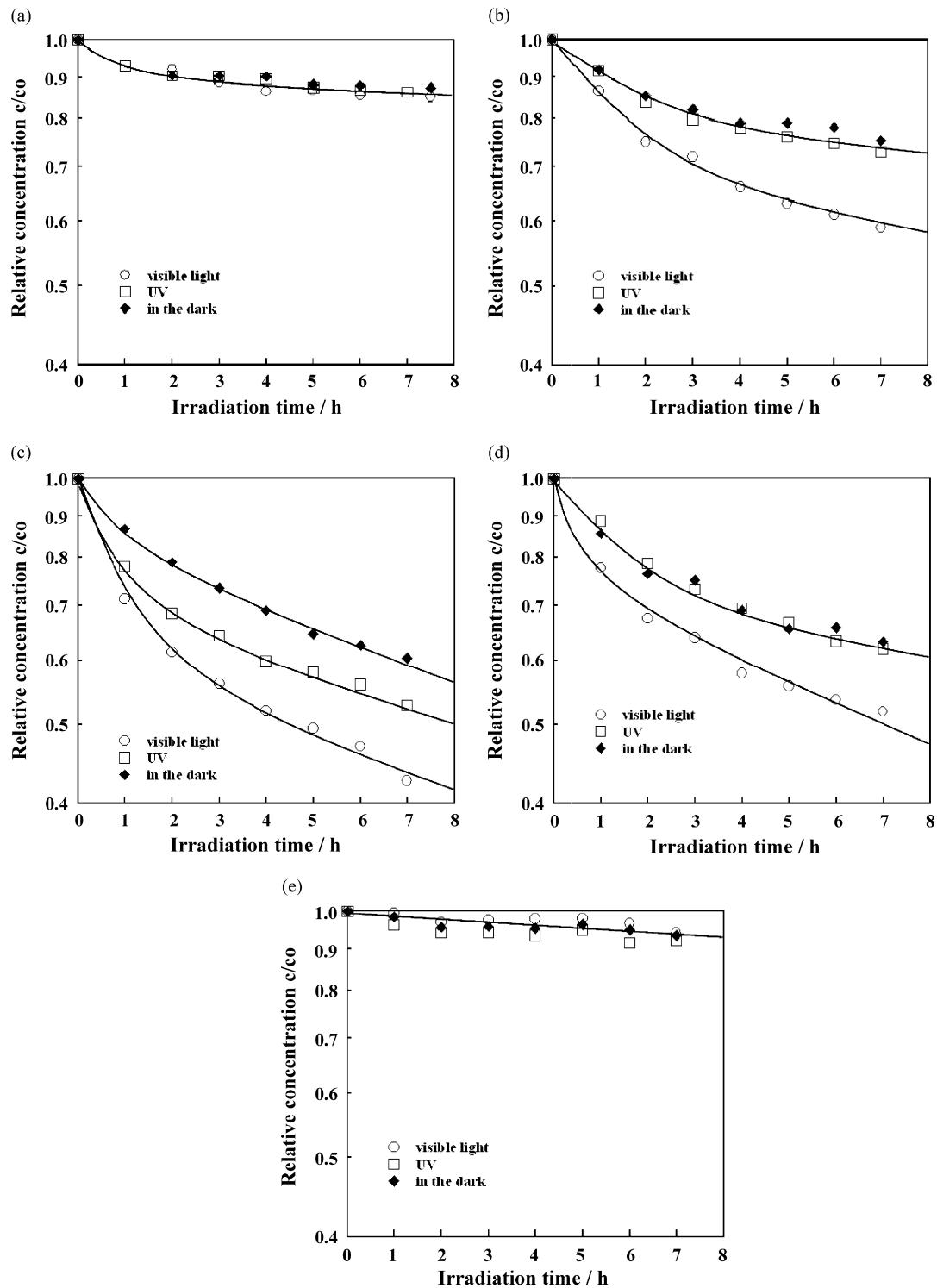


Fig. 5. Degradation and adsorption behaviors of methylene blue: (a) 700 °C-prepared sample; (b) 800 °C-prepared sample; (c) 850 °C-prepared sample; (d) 900 °C-prepared sample; (e) 1000 °C-prepared sample.

visible light, the latter being much faster than the former, in the solutions with two different concentrations of phenol, demonstrating that the sample has adsorptivity for phenol and also photocatalytic activity under visible light. In influence of initial concentrations of phenol solutions of 1 and 10 ppm, the lower initial concentration was found to be the higher photodegradation rate. Oxidation and photodegradation of

phenol under visible light irradiation were confirmed by the detection of reaction products; hydroquinone and catechol, which were known to be intermediate products of phenol oxidation, were detected in the solution by ESI-MS after the irradiation for 2 h, formic, acetic and oxalic acids with degradation of phenol were also generated after 3 h irradiation, and the pH of the solution decreased from 7.4 to 4.9.

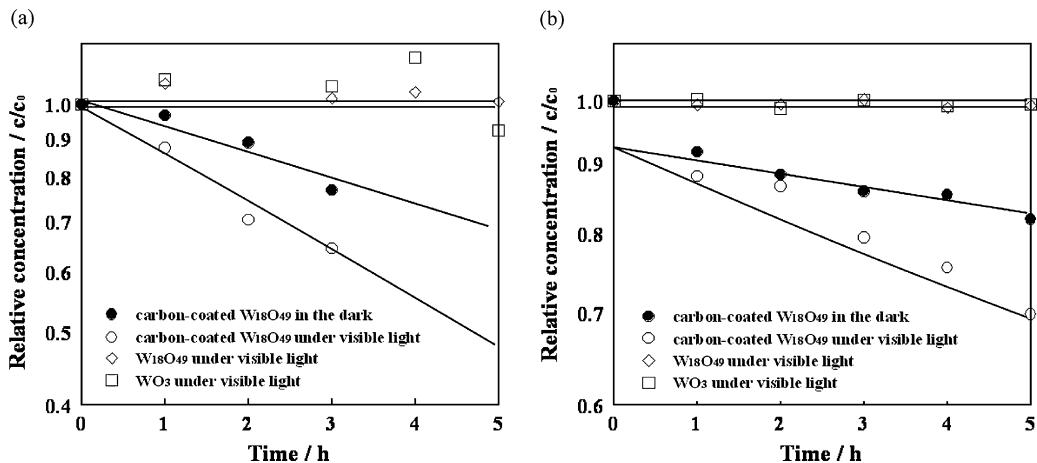


Fig. 6. Decomposition and adsorption behaviors of phenol: (a) in 1 ppm phenol solution and (b) in 10 ppm phenol solution.

3.2.3. Photocatalytic degradation of DMSO

In order to prove the formation of OH radicals under visible light irradiation, which was known to be responsible for photoactivity of anatase-type TiO₂ photocatalyst, the changes in concentration of DMSO and its oxidation product MSA were plotted against visible light irradiation time t under the suspension of carbon-coated tungsten oxide prepared at 800 °C in Fig. 7a. The decrease in concentration of DMSO from 3.45 to 2.91 ppm results in an increase in concentration of MSA from 0 to 0.48 ppm. The relation between the decrease in the concentration of DMSO and the increase in that of MSA can be approximated to be linear, of which slope is almost 1.0, as shown in Fig. 7b.

The present results show that the carbon-coated tungsten oxide, which contains W₁₈O₄₉, produces active OH radicals under visible light, and so it is active for catalytic degradation of different organic compounds under visible light.

3.3. Water solubility of tungsten oxides

The main drawback in WO₃ as visible light active photocatalyst was pointed out to be a high solubility in water.

The solubility of W₁₈O₄₉ into water was preliminary examined in the present work. Carbon-coated tungsten oxide prepared at 800 °C in Ar, which consisted of WO₂ and W₁₈O₄₉, was suspended in water under visible light irradiation for 24 h. XRD patterns of the samples before and after suspension in water are shown in Fig. 8.

After the suspension in water for 24 h, the diffraction peaks corresponding to WO₂ disappear completely, but all diffraction peaks of W₁₈O₄₉ phase remain. In the present system, WO₂ seemed to be oxidized to WO₃ and changed to its hydrolyzed compound WO₃·H₂O, a part of which deposited on catalyst particles, presumably in carbon layer coated. Therefore, W₁₈O₄₉ was supposed to have much smaller solubility for water than WO₂.

4. Discussion

In the present work, visible light activity was observed only on the carbon-coated tungsten oxides prepared at temperatures between 800 and 900 °C, all of which contained W₁₈O₄₉ phase. However, it was not detected on single phase of W₁₈O₄₉ prepared in reducing atmosphere without carbon coating. For

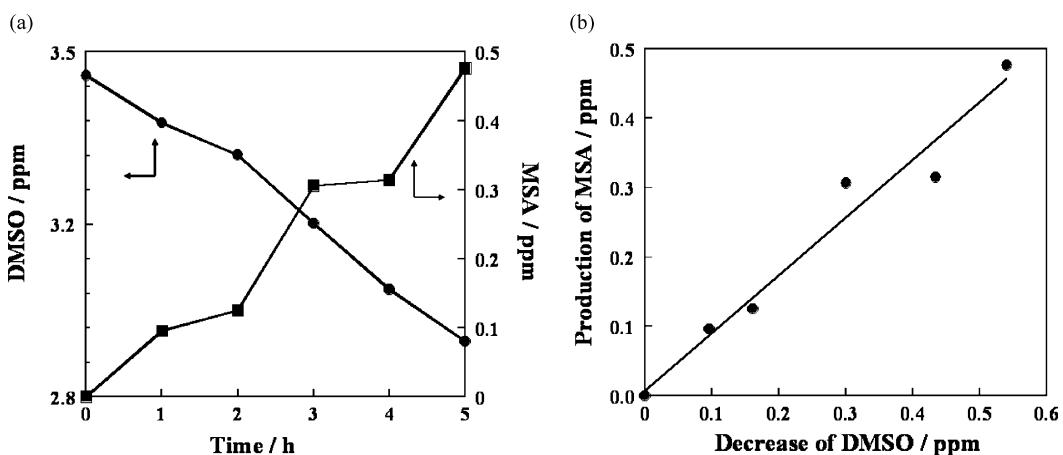


Fig. 7. Changes in the concentrations of DMSO and MSA: (a) changes in concentration of DMSO and MSA and (b) relation between DMSO degraded and MSA formed.

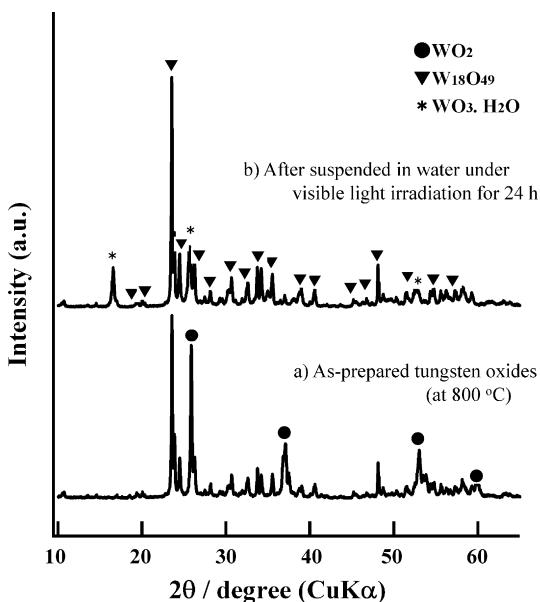


Fig. 8. Change in XRD pattern by dispersion in water under visible light irradiation for the carbon-coated tungsten oxide prepared at 800 °C: (a) after suspended in water under visible light irradiation for 24 h and (b) as-prepared tungsten oxides (at 800 °C).

this experimental result, two reasons might be considered; large size of $W_{18}O_{49}$ particles in the latter and large adsorptivity of the former. The crystals of $W_{18}O_{49}$ with prismatic morphology prepared from WO_3 crystals in reducing atmosphere consisted of much larger particles than those of carbon-coated $W_{18}O_{49}$ (Fig. 2). The larger crystal size is reasonably supposed to give the smaller surface area for the contact with pollutants in the solution even under suspension, which makes the apparent photoactivity the smaller. For $W_{18}O_{49}$, therefore, much higher power of irradiation was supposed to be needed in order to exhibit its photocatalytic activity. The carbon-coated tungsten oxides prepared in the present work had high adsorptivity for methylene blue and phenol, as shown in Figs. 5 and 6, respectively, though no adsorption of phenol was detected on $W_{18}O_{49}$ without carbon coating (Fig. 6). In these carbon-coated samples, the pollutants were supposed to be concentrated at around $W_{18}O_{49}$ particles, much higher concentration than in the solution, which might accelerate the photodegradation of pollutants on the surface of $W_{18}O_{49}$ particles. Therefore, these two factors, small size and carbon coating of $W_{18}O_{49}$ crystals, seem to give detectable activity under visible light.

In order to synthesize small-sized carbon-coated $W_{18}O_{49}$ crystals, it was essential to start from PAT with PVA mixed in solution. Started from the powder mixture of WO_3 and PVA, it was difficult to get small-sized $W_{18}O_{49}$ crystals and also took long time to synthesize its single phase. When K_2WO_4 was used as one of starting materials, which was soluble in water, tungsten carbide WC was obtained, which was useful for the development of pseudo-capacitance in electrochemical capacitor in sulfuric acid electrolyte [29].

The crystal $W_{18}O_{49}$ had the activity not only under visible light but also under UV, as expected from optical diffuse reflectance spectrum (Fig. 4). The activity under UV rays could

experimentally be observed only on the sample prepared at 850 °C, probably because of low strength of UV rays. The formation of active OH radicals under visible light irradiation was experimentally proved through the degradation of DMSO (Fig. 7), suggesting the same mechanism of photoactivity under visible light as that under UV rays, which had been explored mainly on TiO_2 . However, a large difference in strength between UV and visible light (9×10^{-4} and 18 W/cm^2 , respectively) made a quantitative comparison in photoactivity difficult.

A preferential dissolution of WO_2 coexisted with $W_{18}O_{49}$ was experimentally demonstrated (Fig. 8). WO_3 is known to be water soluble, which is a strong drawback as photocatalyst. When $W_{18}O_{49}$ crystals synthesized in reducing atmosphere without carbon coating was suspended in water for 24 h, a weak coloring of the solution but no marked dissolution of the crystals were observed. These preliminary experiments suggested much low water solubility of $W_{18}O_{49}$ crystals.

The $W_{18}O_{49}$ crystal may be considered to have the structure containing oxygen vacancies in ordered arrangement. The visible light activity was also observed on the reduced phases of TiO_2 crystals, Ti_nO_{2n-1} [25,26], where oxygen vacancies existed in ordered manner. In order to give visible light activity to TiO_2 , the doping of foreign atoms, such as C, S, N, Cr, etc., were necessary [6–11], in which some lattice defects, possibly oxygen vacancies, are reasonably supposed to be associated with these dopants in disordered arrangement. These results may suggest that oxygen vacancies in either ordered or disordered arrangement play important role for visible light activity of semiconductive oxides, which requires more detailed studies.

5. Conclusion

Starting from PAT with PVA mixed in solution, carbon-coated $W_{18}O_{49}$ were synthesized in small-sized prismatic crystals through a simple heat treatment in inert atmosphere at around 800 °C. It was proved to have photoactivity under visible light irradiation through the formation of OH^- radicals by using MB, phenol and DMSO. Carbon coating seemed to have various roles; to inhibit the sintering and growth of $W_{18}O_{49}$ crystals to keep them small, and to concentrate pollutants around $W_{18}O_{49}$ crystals by adsorption. Also coated carbon reduces WO_3 to $W_{18}O_{49}$ and finally to WO_2 and metallic W during heat treatment. Since the $W_{18}O_{49}$ phase is formed on the way to complete reduction to metal, a specific range of heat treatment temperature, 750–900 °C in the present condition, was necessary to be selected.

Further investigations on carbon-coated $W_{18}O_{49}$ photocatalyst are needed to determine the exact conditions for its preparation, the most appropriate heat treatment temperature and time, to find out more suitable starting materials and more effective procedure for its preparation. The examination of its use for long period or repeated use is important for its practical application and is possible because carbon-coated samples can be fixed by using organic binder, which was experimentally demonstrated to study the cyclic performance of carbon-coated TiO_2 photocatalysts [30].

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